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# SOME VULCANIZATION TESTS OF GUAYULE RUBBER

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*Bureau of Standards*

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# SOME VULCANIZATION TESTS OF GUAYULE RUBBER

By D. Spence and C. E. Boone

ABSTRACT

This paper gives the results of some physical tests of guayule rubber grown in both Mexico and California. The samples of guayule rubber were obtained from shrub which had been harvested and treated, the rubber being forwarded to the Bureau of Standards. Figures are given showing the properties of different types of guayule rubber and several compounds made with standard plantation crêpes.

Tests were made using "pure gum," zinc oxide, and gas-black formulas and also in formulas where one-half the guayule rubber was replaced with plantation crêpe. Some data are given on the aging properties of compounds based on eight months' exposure to the weather protected from sunlight.

The results indicate that properly prepared guayule rubber will compare favorably with plantation Hevea rubber.

In a paper read before the American Chemical Society at Philadelphia, in September, 1926, several factors which affect the quality and uniformity of guayule rubber were briefly discussed. In the following communication will be found some preliminary physical data bearing on this subject. All the figures here shown were obtained from samples of guayule rubber prepared for comparative tests by the Continental-Mexican Rubber Co. at Torreon, in Mexico. The samples of guayule rubber were obtained from shrub which had been harvested and treated, the rubber being forwarded to the Bureau of Standards. As pointed out in the communication referred to above the guayule shrub and the rubber therein is prone to deterioration after the shrub is cut or pulled from the ground and, in consequence, it is doubtful whether the true value of guayule has ever been determined. The difficulties incidental to the gathering of the shrub from the widely scattered areas of northern Mexico, where it abounds, and the problems of transportation in a country where railroad, not to mention motor truck, transportation is limited, have all had their prejudical effect on the quality and uniformity of the resulting rubber. Not until recently have means been found of preserving the quality of guayule rubber and of preventing the deterioration of the rubber in the shrub while in transit or storage.

It is with the question of the quality of the improved products derived from the guayule shrub by suitable treatment guarding against

deterioration that the present communication has to deal. Vulcanization tests have been made on a number of samples, prepared for the most part from guayule shrub grown in central California, under carefully controlled conditions and shipped to Torreon in Mexico for extraction; some tests will also be found on the native Mexican product, derived from the shrub collected at random from the desert regions of northern Mexico and suitably treated. It should be noted, however, that in either case a considerable period of time, not less than two months, elapsed between the time of harvesting and the time of extraction of the shrub during which certain changes in the rubber in the plant were going on. As the results here show and as experience has taught, maximum improvement in physical quality is only attained when the shrub is treated before the physical degeneration of the rubber therein has taken place.

The means by which gauyule is obtained from the shrub at the present time are as follows: The whole shrub, root as well as branches, is first crushed by a series of crusher rolls in presence of water. After crushing, the mass is fed continuously with additional water to a tube mill or mills. These mills contain flint pebbles and revolve slowly on a horizontal axis. Their action on the shrub depends on the rolling motion of the pebbles in the presence of water and results in a further disintegration of the fiber out of the shrub and the agglomeration, or "worming," of the rubber substance into small, round, spongy particles, which vary in size with the condition of the shrub and the time of milling. The fine particles of rubber, or "worms," being lighter than water, float on the surface of the discharge liquor from these tube mills, while the bulk of the fiber and other impurities sinks and can readily be separated. The rubber "worms," which rise to the surface of the settling tanks into which the liquor from the tube mills is run, are skimmed off and collected. The "worms" are further purified and are then worked into sheets on sheeting rolls, well washed and dried.

In the tests which follow advantage has been taken of some of the most recent developments in rubber compounding. For example, zinc oxide and stearic acid have been used throughout, preliminary determinations having shown that while the acetone soluble substances of guayule rubber appear to produce the dissolution of the zinc oxide to some extent, on the whole better results are obtained when a small amount of a fatty acid, such as stearic, is added to the mix. Diphenylguanidine was used as an accelerator in all tests, except those given in Table 10. It is felt, however, that better results will be attained in the vulcanization of guayule rubber by a study of different organic accelerators under varying conditions.

Compounds of guayule rubber without admixture with other rubber on standard pure gum, zinc oxide, and gas-black formulas

have been made and tested in the usual way; also some tests have been made by substituting one-half of the plantation rubber in a given formula by guayule rubber. In this connection and in order to eliminate the effect of the resins present in the guayule rubber, and thus admit of a better comparison between the rubber of Hevea and that from guayule, a quantity of rubber free from resins was prepared from one of the samples of special guayule by extraction of the latter by means of acetone.

Values for tensile strength and ultimate elongation were determined according to standard procedure, as described in Bureau of Standards Circular No. 232. In regard to the figures for permanent set here given, these were obtained by stretching the test pieces (500 per cent for pure gum compounds and 400 per cent for compounded stocks) for 10 minutes, then releasing and measuring the "set" at intervals until permanent deformation was obtained.

Unless otherwise specified, the formulas used throughout for the testing of these materials were as follows:

| | Pure-gum formula, parts by weight | Zinc-oxide formula, parts by weight | Gas-black formula, parts by weight |
|---|---|---|---|
| Rubber | 100 | 100 | 100 |
| Zinc oxide | 3 | 80 | 28 |
| Gas black | | | 36 |
| Sulphur | 6 | 6 | 5 |
| Stearic acid | 1.5 | 1.5 | 1.5 |
| D. P. G | .5 | .5 | .5 |

The sheets were cured for varying lengths of time at 40 lbs./in.$^2$ steam pressure (141.7° C.) in an open platen vulcanizing press.

In Tables 1 and 2 will be found physical tests of three samples of guayule rubber prepared from the ordinary run of Mexican shrub taken from storage and treated as follows:

(A) Shrub (2 months old), milled immediately after crushing.

(B) Same shrub, milled two weeks after crushing.

(C) Same shrub, milled two weeks after crushing and treated for preservation of shrub.

TABLE 1.—*Mexican wild guayule on pure-gum formula*

| Cure (minutes) | A | | | B | | | C | | |
|---|---|---|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs./in.$^2$* | *Per cent* | *Per cent* | *Lbs./in.$^2$* | *Per cent* | *Per cent* | *Lbs./in.$^2$* | *Per cent* | *Per cent* |
| 30 | 1,925 | 845 | | 1,790 | 825 | | 2,255 | 840 | |
| 45 | 1,975 | 765 | 5 | 2,070 | 780 | 8 | 2,560 | 765 | 7 |
| 60 | 1,965 | 745 | | 2,035 | 745 | | 2,545 | 740 | |
| 75 | 1,945 | 750 | | 1,835 | 710 | | 2,450 | 720 | |

Table 1 shows the deterioration which has occurred and is indicative of the effect of treatment to prevent the deterioration of the shrub.

TABLE 2.—*Mexican wild guayule on zinc oxide formula*

| Cure (minutes) | A | | | B | | | C | | |
|---|---|---|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* |
| 45 | 1,990 | 805 | --- | 1,890 | 740 | --- | 2,590 | 775 | --- |
| 60 | 2,040 | 755 | 11 | 1,845 | 695 | 24 | 2,675 | 730 | 17 |
| 75 | 1,985 | 725 | --- | 1,905 | 670 | --- | 2,555 | 715 | --- |

The effect of the treatment of the shrub is likewise apparent (Table 2), using a zinc oxide formula.

In Table 3 will be found figures for the product from the cultivated shrub grown in California and shipped to Mexico for extraction. "A" represents the product extracted as received and "B" the same product extracted after crushing and treatment for the betterment of the rubber.

TABLE 3.—*Cultivated Californian guayule rubber on zinc oxide formula*

| Cure (minutes) | A | | B | |
|---|---|---|---|---|
| | Tensile strength | Elongation | Tensile strength | Elongation |
| | *Lbs./in.²* | *Per cent* | *Lbs./in.²* | *Per cent* |
| 30 | --- | --- | 2,670 | 740 |
| 45 | 1,940 | 740 | 2,650 | 715 |
| 60 | 2,120 | 715 | 2,430 | 645 |
| 75 | 2,100 | 685 | 2,410 | 635 |
| 90 | 1,690 | 620 | --- | --- |

The results in the above table further show the effect of treating the shrub to prevent deterioration. A marked improvement of the tensile properties is apparent.

In the following tables (4, 5, and 6) are given physical tests on a lot of Californian cultivated shrub shipped to Mexico and extracted two months later. This lot of about 80 tons of shrub was run through in the usual way, except that part of the lot was treated to better preserve the quality of the rubber. Tests were made on air-dried and vacuum-dried samples, using pure gum, zinc oxide, and on gas-black formulas.

TABLE 4.—*Californian cultivated guayule on pure gum formula*

| Cure (minutes) | C. G. V.[1] | | | C. G. P. A.[2] | | | C. G. P. V.[3] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* |
| 15 | --- | --- | --- | 2,310 | 845 | --- | 2,535 | 800 | --- |
| 30 | 1,630 | 905 | --- | 2,395 | 740 | 11 | 2,400 | 695 | 12 |
| 45 | 1,990 | 855 | --- | 2,290 | 695 | --- | 2,315 | 685 | --- |
| 60 | 2,035 | 815 | 8 | --- | --- | --- | --- | --- | --- |

[1] C. G. V., Californian cultivated guayule rubber, vacuum dried.
[2] C. G. P. A., Californian cultivated guayule rubber, treated and air dried.
[3] C. G. P. V., Californian cultivated guayule rubber, treated and vacuum dried.

TABLE 5.—*Californian cultivated guayule on zinc oxide formula*

| Cure (minutes) | C. G. V.[1] | | | C. G. P. A.[2] | | | C. G. P. V.[3] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs. /in.²* | *Per cent* | *Per cent* | *Lbs. /in.²* | *Per cent* | *Per cent* | *Lbs. /in.²* | *Per cent* | *Per cent* |
| 30 | 1,530 | 865 | | 2,300 | 755 | 17 | 2,295 | 745 | 18 |
| 45 | 1,890 | 835 | | 2,080 | 685 | | 2,190 | 675 | |
| 60 | 1,975 | 770 | 17 | 2,080 | 655 | | 2,030 | 635 | |
| 75 | 1,925 | 765 | | 1,830 | 605 | | 2,245 | 680 | |

[1] C. G. V., Californian cultivated guayule rubber, vacuum dried.
[2] C. G. P. A., Californian cultivated guayule rubber, treated and air dried.
[3] C. G. P. V., Californian cultivated guayule rubber, treated and vacuum dried.

TABLE 6.—*Californian cultivated guayule on gas-black formula*

| Cure (minutes) | C. G. V.[1] | | | C. G. P. A.[2] | | | C. G. P. V.[3] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs. /in.²* | *Per cent* | *Per cent* | *Lbs. /in.²* | *Per cent* | *Per cent* | *Lbs. /in.²* | *Per cent* | *Per cent* |
| 30 | | | | | | | 2,510 | 715 | |
| 45 | 1,995 | 790 | | 2,430 | 690 | | 2,525 | 680 | 27 |
| 60 | 2,135 | 765 | | 2,620 | 655 | 27 | 2,475 | 655 | |
| 75 | 2,145 | 765 | 27 | 2,615 | 625 | | 2,440 | 645 | |
| 90 | 2,020 | 720 | | 2,355 | 625 | | | | |

[1] C. G. V., Californian cultivated guayule rubber, vacuum dried.
[2] C. G. P. A., Californian cultivated guayule rubber, treated and air dried.
[3] C. G. P. V., Californian cultivated guayule rubber, treated and vacuum dried.

The results shown in the above tables confirm the previous results. In the three cases, using pure gum, zinc oxide, and gas-black formulas, better properties are obtained with the rubber from the treated shrub.

In the following tables (7, 8, and 9) will be found a comparison of the tensile and elongation properties of guayule rubber with those of a sample of first latex crêpe on the three test formulas used throughout. For the purpose of the test a large quantity of the Californian grown rubber, treated to better preserve the inherent quality of the rubber and tested under Tables 4, 5, and 6, was first extracted with acetone while still in the "worm" stage. The acetone soluble substances of the rubber were reduced to less than 1 per cent, and the rubber when air-dried was in the form of a hard, dry crêpe, with no signs of stickiness.

TABLE 7.—*Comparison of Californian cultivated guayule with first latex crêpe on pure gum formula*

| Cure (minutes) | First latex crêpe | | | Extracted guayule rubber | | |
|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* |
| 30 | 2,680 | 785 | | 2,810 | 725 | |
| 45 | 2,885 | 750 | 3 | 3,220 | 715 | 10 |
| 60 | 2,860 | 765 | | 2,900 | 660 | |
| 75 | 2,435 | 785 | | | | |

TABLE 8.—*Comparison of Californian cultivated guayule with first latex crêpe on zinc oxide formula*

| Cure (minutes) | First latex crêpe | | | Extracted guayule rubber | | |
|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* |
| 30 | 3,125 | 695 | ---- | 2,650 | 730 | ---- |
| 45 | 3,430 | 680 | 11 | 3,000 | 685 | 12 |
| 60 | 3,275 | 665 | ---- | 2,845 | 665 | ---- |
| 75 | 2,770 | 590 | ---- | 2,780 | 675 | ---- |

TABLE 9.—*Comparison of Californian cultivated guayule with first latex crêpe on gas-black formula*

| Cure (minutes) | First latex crêpe | | | Extracted guayule rubber | | |
|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* |
| 45 | 3,255 | 650 | ---- | 2,945 | 600 | ---- |
| 60 | 3,800 | 635 | 17 | 3,450 | 570 | 27 |
| 75 | 3,855 | 610 | ---- | 3,375 | 540 | ---- |

The guayule rubber when extracted with acetone shows tensile properties comparable with plantation crêpe. Using the pure gum formula the properties are enhanced, whereas the zinc oxide and gas-black compounds are slightly poorer in their physical properties.

In Table 10 will be found a comparison of plantation crepe with acetone extracted and processed Californian guayule, also with the same materials without extraction. This comparison was made on the following pure gum formula.

| | Parts by weight |
|---|---|
| Rubber | 100.0 |
| Zinc oxide | 3.0 |
| Sulphur | 2.0 |
| Tetramethylthiuramdisulphide | .34 |
| Ethylidine aniline | .50 |

TABLE 10.—*Comparison of Californian guayule with plantation crêpe on pure gum formula*

| Cure (minutes) | Plantation crêpe | | Extracted and processed guayule | | Processed guayule | |
|---|---|---|---|---|---|---|
| | Tensile strength | Elongation | Tensile strength | Elongation | Tensile strength | Elongation |
| | *Lbs./in.²* | *Per cent* | *Lbs./in.²* | *Per cent* | *Lbs./in.²* | *Per cent* |
| 5 | 4,270 | 730 | 3,800 | 685 | 2,665 | 830 |
| 10 | 4,280 | 670 | 4,105 | 650 | 2,640 | 800 |
| 15 | 3,860 | 655 | 3,755 | 630 | 2,110 | 770 |
| 20 | 3,350 | 625 | 3,450 | 615 | 1,845 | 745 |

The extracted guayule in this case possesses tensile properties practically equal to those of the plantation crêpe.

In Table 11 will be found a comparison of plantation crêpe with Californian grown guayule on a replacement basis. In this case the standard zinc oxide formula was used, and 50 per cent of the plantation crêpe contained in the original mixing (No. 1) was replaced by an equal weight of acetone extracted and treated guayule in No. 2 and a like amount of the original Californian rubber from which the extracted product was prepared in No. 3.

TABLE 11.—*50 per cent replacement of plantation crêpe by Californian-grown guayule (extracted and unextracted) on standard zinc oxide formula*

| Cure (minutes) | Plantation crêpe (No. 1) | | | Californian-grown guayule | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Extracted (No. 2) | | | Unextracted (No. 3) | | |
| | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set | Tensile strength | Elongation | Permanent set |
| | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* | *Lbs./in.²* | *Per cent* | *Per cent* |
| 30 | 1,725 | 675 | ---------- | 2,000 | 670 | ---------- | 2,515 | 705 | ---------- |
| 45 | 3,150 | 665 | 11 | 3,110 | 640 | 12 | 2,890 | 645 | 14 |
| 60 | 3,175 | 625 | 17 | 2,995 | 610 | 17 | 2,525 | 610 | 20 |

The figures here cited make no pretense to be a complete evaluation of the physical properties of guayule rubber. They represent merely the results of a preliminary and somewhat superficial examination of the product from the guayule shrub grown under agricultural conditions in California and prepared by the best methods as yet possible. In the first place, all the samples of rubber tested were obtained from shrub 2 months or more old before extraction; it is probable that better results would have been obtained from the same shrub by prompt treatment of it to inhibit deterioration. The tests, furthermore, have all been made on test formulas and under vulcanizing conditions chosen more or less arbitrarily, without regard to the specific requirements for the best vulcanization of this rubber. There is still much left to be determined in this connection.

Notwithstanding the limitations of necessity imposed on the results so far, the tensile and elongation properties of the products prepared from the guayule shrub by suitable treatment indicate that, when properly prepared, the rubber from guayule will compare favorably with that from Hevea and can be used to a large extent as a direct equivalent therefor without appreciable diminution of the tensile elongation product. The great improvement in the product from guayule to be derived from the successful development of means to prevent the deterioration of the rubber in the shrub is clearly indicated, and it is by no means to be assumed that the last word has been said in this connection.

The values obtained for permanent set are high by comparison with similar samples of plantation rubber, but here, again, much work remains to be done before definite conclusions can be reached.

Guayule rubber mixes readily with compounding ingredients, because it appears to have a greater capacity for dispersing them than ordinary rubber. This fact calls for a complete investigation of the best means for the utilization of the product to the best advantage.

Since the foregoing tests were made aging tests have been completed upon some of the vulcanized samples after eight months of storage in a box exposed to the outside temperatures, but protected from the light. The results before and after aging are given in Table 9.

TABLE 9

| | Reference | Cure | Original test | | After 8 months | |
|---|---|---|---|---|---|---|
| | | | Tensile strength | Elongation | Tensile strength | Elongation |
| | | *Minutes* | *Lbs./in.²* | *Per cent* | *Lbs./in.²* | *Per cent* |
| Table 1 | A | 45 | 1,975 | 765 | 1,420 | 685 |
| | B | | 2,070 | 780 | 1,110 | 570 |
| | C | | 2,560 | 765 | 2,115 | 665 |
| Table 4 | C. G. V | 45 | 1,990 | 855 | 1,590 | 770 |
| | | 60 | 2,035 | 815 | 1,550 | 710 |
| | C. G. P. A | 15 | 2,310 | 845 | 2,095 | 770 |
| | | 30 | 2,395 | 740 | 1,975 | 705 |
| | C. G. P. V | 30 | 2,535 | 800 | 2,400 | 690 |
| | | 45 | 2,400 | 695 | 2,170 | 650 |
| Table 5 | C. G. V | 45 | 1,890 | 835 | 1,735 | 700 |
| | | 60 | 1,975 | 770 | 1,640 | 645 |
| | C. G. P. A | 30 | 2,300 | 755 | 2,055 | 675 |
| | | 45 | 2,280 | 685 | | |
| | C. G. P. V | 30 | 2,295 | 745 | 2,195 | 650 |
| | | 45 | 2,190 | 675 | 1,995 | 615 |
| Table 6 | C. G. V | 60 | 2,135 | 765 | 1,440 | 580 |
| | | 75 | 2,145 | 765 | 1,280 | 510 |
| | C. G. P. A | 45 | 2,430 | 690 | 1,910 | 575 |
| | | 60 | 2,620 | 655 | 1,810 | 500 |
| | C. G. P. V | 45 | 2,525 | 680 | 2,095 | 580 |
| Table 7 | First latex | 45 | 2,885 | 750 | 2,465 | 655 |
| | | 60 | 2,860 | 705 | 2,650 | 695 |
| | Guayule | 30 | 2,810 | 725 | 2,320 | 660 |
| | | 45 | 3,100 | 715 | 2,495 | 615 |
| Table 8 | First latex | 30 | 3,125 | 695 | 2,915 | 700 |
| | | 45 | 3,430 | 680 | 2,860 | 650 |
| | Guayule | 30 | 2,650 | 730 | 2,550 | 640 |
| | | 45 | 3,000 | 685 | 2,565 | 605 |

These results show the usual dropping off in tensile and elongation properties with aging. They also show the marked improvement in this regard brought about by suitable treatment of the shrub. The drop in tensile and elongation in the case of the treated product compares favorably with the results obtained with first latex crêpe under similar conditions. (Tables 7 and 8.)

WASHINGTON, June 20, 1927.